

Freeze–Thaw Effects on Phosphorus Loss in Runoff from Manured and Catch-Cropped Soils

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ABSTRACT

Concern over nonpoint source P losses from agricultural lands to surface waters in frigid climates has focused attention on the role of freezing and thawing on P loss from catch crops (cover crops). This study evaluated the effect of freezing and thawing on the fate of P in bare soils, soils mixed with dairy manure, and soils with an established catch crop of annual ryegrass (*Lolium multiflorum* L.). Experiments were conducted to evaluate changes in P runoff from packed soil boxes (100 by 20 by 5 cm) and P leaching from intact soil columns (30 cm deep). Before freezing and thawing, total P (TP) in runoff from catch-cropped soils was lower than from manured and bare soils due to lower erosion. Repeated freezing and thawing significantly increased water-extractable P (WEP) from catch crop biomass and resulted in significantly elevated concentrations of dissolved P in runoff (9.7 mg L⁻¹) compared with manured (0.18 mg L⁻¹) and bare soils (0.14 mg L⁻¹). Catch crop WEP was strongly correlated with the number of freeze–thaw cycles. Freezing and thawing did not change the WEP of soils mixed with manures, nor were differences observed in subsurface losses of P between catch-cropped and bare soils before or after manure application. This study illustrates the trade-offs of establishing catch crops in frigid climates, which can enhance P uptake by biomass and reduce erosion potential but increase dissolved P runoff.

THE CONTROL of nonpoint-source nutrient pollution, particularly P and N, represents a major environmental challenge for agriculture in Europe and North America due to widespread problems of surface water eutrophication and ground water contamination (Carpenter et al., 1998; Withers and Lord, 2002). Large gains have been made in implementing management practices to reduce losses of individual nutrients from agricultural soils, but successful control of one nutrient may unintentionally exacerbate losses of another.

Catch crops, synonymous with cover crops, are widespread in Scandinavia, where they have been heavily promoted for water quality protection (Ulén, 1997; Molteberg and Tangsvén, 2002). For instance, since 1999 in Norway, there has been an increase in subsidies allocated to farmers to plant catch crops (Lundekvam et al., 2003). The primary objective of promoting catch crops is to minimize nitrate N leaching after summer crops have been harvested (Meisinger et al., 1991; Bergström and Jokela, 2001). Because catch crops are unfertilized,

they incorporate available soil nutrients into their biomass, hence the name *catch crop*, lowering the amount of N available to leaching within the rooting zone. In addition, catch crops have been shown to decrease soil erosion potential and associated particulate P losses compared with autumn plowed soils and even compared with soils under minimum tillage (Sharpley and Smith, 1991; Lundekvam et al., 2003).

The benefit of catch crops to dissolved P transport is less clear than for erosion and nitrate N leaching, with some authors suggesting that catch crops may even increase dissolved P losses (Uhlen, 1989; Børresen and Uhlen, 1991). The basis for this opinion is that catch crops concentrate P above ground, some of which may become available to runoff. Under field conditions, annual ryegrass, a common catch crop in northern agroecosystems, contains 1.7 to 7 kg ha⁻¹ of total P (TP) (Ulén, 1997; Molteberg and Tangsvén, 2002), with 60 to 80% of plant P in inorganic form (Jones and Bromfield, 1969; Sharpley and Reed, 1982). Annual ryegrass contains more P than other less common catch crops, like white clover (*Trefolium repens* L.) and fescue grass (*Festuca pratensis* Huds.) (Miller et al., 1994; Sturite and Henriksen, 2002). Furthermore, Pierzynski and Logan (1993) found differences in the ability of various crops to recover soil P, resulting in a range of aboveground biomass P.

Under certain conditions, the inorganic P in catch crops may be released to water, contributing to the transfer of P to surface waters (Timmons et al., 1970; Sharpley and Smith, 1991; Miller et al., 1994). Miller et al. (1994) showed that much inorganic P was leached from ryegrass catch crops exposed to simulated rainfall after freezing, but only minimal organic P was leached. Gburek and Broyan (1974) compared sequential laboratory leachings of orchardgrass (*Dactylis glomerata* L.) with seasonal differences in water quality in a watershed in Pennsylvania and concluded that contributions of dissolved P from vegetation could account for elevated concentrations of P in runoff. Elsewhere, Sharpley (1981) found that an increase in the age of cotton (*Gossypium hirsutum* L.), sorghum (*Sorghum sudanense* Stapf.), and soybean [*Glycine max* (L.) Merr.] resulted in greater contributions of dissolved P from plant leaves to runoff, accounting for increases in runoff P by 20 to 60%.

In cold climates, freezing and thawing can play an additional role in dissolved nutrient transport. Each freezing event damages plant cells, with lysed cells potentially releasing dissolved P (White, 1973; Uhlen, 1989). For instance, in a field experiment Børresen and Uhlen (1991) observed an increase in the concentration of dissolved

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Abbreviations: DRP, dissolved reactive phosphorus; FTC, freeze/thaw cycle; ICP-AES, inductively coupled plasma–atomic emission spectrometry; SS, suspended solids; TP, total phosphorus; WEP, water extractable phosphorus.

reactive P (DRP) in runoff from ryegrass plots from 0.15 mg L^{-1} before freezing to 0.68 mg L^{-1} after freezing. In a pot experiment with annual ryegrass, Molteberg et al. (2004) found that 22% of the plant P content was lost through leaching, with most of this loss occurring (90%) in late (January–April) winter, owing to plant physiological changes (White, 1973).

Freezing and thawing can also influence the release of P from the soil itself (Mack and Barber, 1960). Several studies have shown that freezing significantly increases water-extractable P (WEP) in both mineral and organic soils (Walworth, 1992; Vaz et al., 1994). On the other hand, direct chemical effects of freeze–thaw episodes such as precipitation reactions combined with changes in microbial activity linked to physical changes in soil structure may cause decreases in available nutrients (Lehrsch, 1998). These changes are described in detail by Vaz et al. (1994), who found organic soils to be the most susceptible to freezing effects, concluding that increases in P solubility were related to dissolution of organic compounds and disruption of plant cells.

Model simulations of future changes in climate suggest that larger temperature fluctuations can be expected in the Scandinavian region than the global mean, which, in turn will affect the structure of freeze–thaw events (Rummukainen et al., 2003). In particular, the number of freeze–thaw cycles (FTCs) experienced during Scandinavian winters may change, in some areas causing an increased number of FTCs (T.E. Skaugen, www.met.no, personal communication, 2004). Indeed, Vaz et al. (1994) found the frequency of FTCs to be positively correlated to WEP in soil.

The objective of this study is to evaluate the effect of freezing and thawing on P loss in surface and subsurface flow from catch-cropped soils. Three experiments were conducted to assess P fate in bare, manured, and catch-cropped soils as a function of FTCs. First, an incubation experiment was conducted to evaluate the effect of freezing on changes in soil P fractions, as well as changes in the availability of P in catch-crop biomass. Second, an experiment was conducted to evaluate the effects of freezing on P in runoff from catch-cropped, manured, and bare soils. Finally, the role of freezing on P leaching was evaluated with bare, catch-cropped, and manured soil columns.

MATERIALS AND METHODS

Soil and Manure Collection

Surface horizons (0–20 cm) of Berks (loamy-skeletal, active, mesic Typic Dystrochrept) and Watson (fine-loamy, active, mesic Typic Fragiudult) soils were collected from the USDA-ARS FD-36 research watershed in Pennsylvania, USA, air-dried, sieved (1.4 cm), and mixed thoroughly. To ensure homogeneity of individual soil samples, the effectiveness of mixing was evaluated by conducting Mehlich-3 P extraction (Mehlich, 1984) on six subsamples from each soil and determining the coefficient of variation (standard deviation divided by mean Mehlich-3 P concentration) for each soil. For both soils, mixing was conducted until the coefficient of variation in Mehlich-3 P was <0.05 .

Dairy manure containing feces, urine, and saw-dust bedding

was collected from the Pennsylvania State University Dairy Center (University Park, PA). The dairy manure was from lactating Friesian-style dairy cows and was scraped from the concrete floor of a free stall barn. As such, the manure was representative of manure that would be spread under daily-haul conditions common to small dairy farms without manure storage facilities. The manure was collected 5 d before the soil incubation and runoff experiments and thoroughly mixed by stirring. A 1-L subsample was obtained and stored at 4°C before analysis.

Incubation Experiments

Three incubation experiments were conducted to assess the effects of freezing and thawing on P fractions in bare soil, soil mixed with manure, and plant material. The first incubation experiment was designed to assess the effects of freezing on soil P related to manure application rate; 250-mL plastic cups were filled with either Watson or Berks soils. The soils were amended with dairy manure equivalent to application rates of 0, 40, and 80 kg TP ha^{-1} (assuming a 20-cm soil depth and bulk density of 1.3 g cm^{-3}). Application rates of 40 and 80 kg TP ha^{-1} equate roughly to recommended P- and N-based (200 kg N ha^{-1}) applications, respectively (Beegle, 2001). Manure was mixed with soil to simulate incorporation of land-applied manure.

Soils in the first incubation experiment were incubated for 21 d in a greenhouse ($25\text{--}35^{\circ}\text{C}$) during which they were subjected to the same irrigation regime as the packed soils in the runoff experiment described below. After the 21-d incubation, soil cups were subjected to either 0, 1, or 8 FTCs. Controls were not frozen, but stored at 4°C . A single FTC consisted of 8 d at -18°C and followed by 12 h at 10°C . Before starting the freezing treatments, soil moisture content was increased to field capacity, approximately 35 and 31% gravimetric water content for Watson and Berks soils, respectively. All incubation treatments were performed in triplicate.

The second incubation experiment was designed to assess the effect of FTC duration and frequency on the release of P from catch crop biomass. Ryegrass was seeded to the Watson soil in 250-mL plastic cups at a rate of 50 g m^{-2} and grown for 21 d in a greenhouse, receiving the same temperature and hydrologic regime as Incubation Experiment 1 and the runoff box experiment. After 21 d, the ryegrass was harvested (clipped at the soil surface). Plant residues (three replicates) were subjected to zero, one, two, four, six, or eight FTCs, each consisting of 12 h at -18°C and 12 h at 10°C . After freezing, the samples were stored at 5°C until all treatments were ended. One set of plant residues (three replicates) was subjected to a single freezing treatment consisting of 8 d at -18°C followed by 12 h at 10°C .

A third incubation experiment was conducted in parallel with the runoff experiment to provide information on transformation and translocation of P with various treatments. Runoff boxes (1 m long by 20 cm wide) were sectioned into five 20 by 20 cm compartments (0.04 m^2) using plastic dividers. Compartments were packed with Watson soil to a depth of 5 cm to achieve a bulk density of approximately 1.3 to 1.5 g cm^{-3} . Each compartment was subjected to the three management treatments evaluated in the runoff study (catch crop, incorporated manure, bare soil). These boxes were treated in an identical fashion to those used in the runoff study, described below, up to the point of rain simulation. At that time, the contents of each compartment were collected for laboratory analysis, with samples stratified by depth (0–1, 1–3, and 3–5 cm) to assess differences in P fractions between treatments at the time of runoff.

Runoff Experiment

A runoff experiment was conducted with the Watson soil used in the incubation experiment, following a modified version of the National Phosphorus Research Project's indoor runoff box protocol (see Kleinman et al., 2004). The protocol employs stainless steel runoff boxes, 1 m long, 20 cm wide, and 5 cm deep with rear and side walls 2.5 cm higher than the soil surface (Kleinman et al., 2002a). Watson soil was packed into runoff boxes equipped with watertight bases to achieve a bulk density of 1.3 to 1.5 g cm⁻³. To ensure that freezing and thawing of the runoff boxes occurred from the soil surface downward, as would occur in field soils, the side walls and bottoms of each runoff box were covered with 7.5 cm of Dow Styrofoam insulation.¹

Three management treatments were evaluated: catch crop, incorporated manure, and bare soil. All three treatments were initiated on the same day. For the catch crop treatment, annual ryegrass was established in the soil boxes. Seeding was conducted at a rate of 50 g m⁻². To aid in catch crop establishment, a single post-seeding application of ammonium nitrate (~20 kg N ha⁻¹) was conducted. In the manure application treatment, dairy manure was thoroughly homogenized and mixed with soil in the runoff boxes at a TP application rate equivalent to 80 kg P ha⁻¹. A bare soil treatment (no manure application and no catch crop) served as a control. During growing of the catch crop, all boxes were incubated in a greenhouse (25–35°C) for 21 d and irrigated to keep the soil moist. Irrigation was performed manually every 1 to 2 d with a maximum of 1 cm water applied each time.

Twenty-one days after the catch crops were planted, all soil boxes (catch crop, manured soil, and bare soil) were subjected to a rainfall-runoff event. Following the event, soil boxes were subjected to eight freeze-thaw cycles or to a control (no freezing) regime. Each freeze-thaw cycle consisted of 12 h at -18°C and 12 h at 10°C and finished by 12 h freezing; in the control, the boxes were stored continuously at 10°C. All soil boxes were stored for the same period of time (8 d) so that the unfrozen control boxes remained in storage at 10°C until the eight-cycle treatment was completed. After the 8 d, half of the frozen boxes (a) were thawed at 10°C for 12 h and the other half (b) remained frozen for these 12 h, giving two soil conditions (a and b) at start of the rain simulation. Rainfall-runoff events were performed on a and b boxes immediately and after 12 h when all boxes were thawed. All treatments on runoff boxes were performed in duplicate.

Rain simulations were conducted at 25°C using deionized water (EC = 36 µS, DRP < 0.05 mg L⁻¹). Simulated rain was applied to inclined (3%) soil runoff boxes using a TeeJet ½ HH SS 24 WSQ nozzle (Spraying Systems Co., Wheaton, IL) placed approximately 3.1 m above the soil surface (Humphry et al., 2002). At this height, rainfall achieves >90% terminal velocity. Rainfall intensity was 3.0 cm h⁻¹ and had a coefficient of uniformity >0.86 within the 2 by 2 m area directly below the nozzle where the boxes were placed. Runoff was collected for 30 min via a gutter, equipped with a canopy to exclude direct input of rainfall and inserted at the lowest edge of the runoff box. Following each rainfall, runoff water was thoroughly stirred to resuspend settled particles and a subsample immediately filtered (0.45 µm).

Leaching Experiment

To evaluate differences in P leaching from cover cropped, bare, and manured soils, an experiment was designed using

intact 15-cm diameter and 30-cm deep soil columns. Ten Watson and 10 Berks columns were collected. Collection of the soil columns followed the method of McDowell and Sharpley (2001b). Briefly, 15-cm diameter PVC pipe (Schedule 40) was driven into the soil to a depth of 30 cm with a drop-hammer, with care taken not to allow the hammer to come into contact with the soil surface to avoid surface compaction. Columns were excavated from the side, and the column was tipped slightly to break contact with underlying soil along natural ped faces, then removed. The bottom of the column was then supported by a layer of cheese cloth and a PVC cap, filled with fiberglass wool to maintain moderate pressure between the cap and the layer of cheese cloth or bottom of soil column. The PVC cap was sealed to the bottom cylinder with silicone. To allow drainage, a hole was drilled into the center of the cap and fitted with a 1-cm PVC nipple that could be inserted into a plastic collection container (Kleinman et al., 2003; McDowell and Sharpley, 2004). This design ensured free drainage throughout the leaching experiment, minimizing the possibility of reducing conditions developing in the soil columns.

A series of irrigation events was imposed on the soil columns to directly assess P leaching as related to freezing and thawing. The experiment was initiated by leaching all soil columns for 72 h. Soil columns were irrigated with a Raindrip R580 Drip Watering Soaker system (Raindrip, Chatsworth, CA) delivering water at 0.6 cm h⁻¹ every 6 h for a 72-h period (7.2 cm). The irrigation rate was lower than the reported range of infiltration capacities of Watson and Berks soils of 15 to 1.2 cm h⁻¹ (Eckenrode, 1985). After the initial leaching event, annual ryegrass was planted in half (five) of the Berks and Watson soil columns, with seeding and N fertilizer rates following those reported for the runoff experiments. Two weeks after the catch crop had developed, all columns (catch-cropped and bare) were subjected to a second leaching event. Following this event, soil columns were transported to a cooler where they underwent eight FTCs at -18 and 10°C, 12 h each, as described for the runoff experiment. Columns were then subjected to a third (post-freezing) leaching event. After the third leaching, manure was applied to the surface of 8 of the 10 Berks and 10 Watson soil columns at a rate equivalent to 80 kg P ha⁻¹. Two days after manure application, soil columns were leached for a fourth and final time.

Laboratory Analyses

Soils

All soils were air-dried (25°C) before analysis. Water-extractable P was determined by end-over-end shaking 2.0 g of soil with 20 mL of distilled water for 1 h at 25°C. Total P was determined by modified, semi-micro Kjeldahl acid digestion (conc. H₂SO₄), with K₂SO₄ to raise the temperature of digestion and CuSO₄ to promote oxidation of organic matter (Bremner, 1996). Soils were analyzed for Mehlich-3 P by shaking 2.5 g of soil with 25 mL of Mehlich-3 solution (0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.015 M NH₄F + 0.013 M HNO₃ + 0.001 M EDTA) for 5 min (Mehlich, 1984). Phosphorus concentration in Mehlich-3 extracts was determined by modified Murphy and Riley (1962) method, with λ = 712 nm.

Total soil C was determined by elemental analyzer (EA 1110, CE Elantech, Lakewood, NJ). Soil cation exchange capacity (CEC) was calculated from sum of cations, determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis of the Mehlich-3 extract (Ross, 1995). Soil pH was determined by mixing air-dry soil with distilled water (5 g:5 mL). Particle-size analysis was conducted on bulk samples by the hydrometer method (Gee and Bauder, 1986). Field

¹ Mention of trade names does not imply endorsement by the USDA.

moist water content was determined at 10 kPa according to Klute (1986).

Runoff and Leachate Water

Unfiltered water samples were analyzed for total P by alkaline persulfate digestion (Bremner, 1996) and for suspended solids (SS) after evaporating 200 mL of runoff water at 105°C. Filtered (<0.45 µm) samples were analyzed for dissolved reactive P (DRP). Phosphorus in all filtrates and neutralized digests was determined by modified Murphy and Riley (1962) method.

Manure and Plant Samples

Total P in manure was determined by Kjeldahl digestion, as described above. Manure WEP was determined by agitating (end-over-end shaker, 16 rpm) 10 g of fresh manure with 125 mL deionized water (solution/dry matter, 84:1) for 2 h, and filtering the mixture through Whatman no. 42 paper filter. Dry matter content of plant material and manure was determined by drying samples at 60°C for 48 h. Plant WEP was determined by shaking triplicate 0.4-g samples with 80 mL of distilled water for 1 h at 25°C. Total plant P content was determined on dried material ground to pass a 60-µm mesh sieve by digestion of triplicate 0.25-g samples with 3 mL of H₂SO₄ following organic matter oxidation by hot H₂O₂ (Van Lierop, 1976). Again, modified Murphy and Riley (1962) was used for all P determinations. Both WEP and TP of manure and plant samples are reported on a dry-weight equivalent basis.

Statistical Analysis

Data were analyzed for normality by SAS's univariate procedure. Data that were not normally distributed (i.e., runoff and leachate DRP and TP) were analyzed by Kruskal-Wallis test. Remaining data were evaluated by ANOVA, with LSDs to compare individual means. All data were analyzed using SAS, version 8.1 (SAS Institute, 1999). Differences discussed in the text were significant at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Properties of Soil, Manure, and Ryegrass

The two soils had comparable Mehlich-3 P concentrations (Table 1), well in excess of crop P requirements (Beegle, 2001), owing to long histories of manure application (Gburek et al., 2000). The Watson soil had a higher clay content than the Berks, equating to a higher P sorption capacity, as reported by McDowell et al. (2001), and higher erosion potential. Total C concentration was higher in the Berks than Watson soil, contributing to the difference in erosion potential of the two soils.

Dry matter content (15%) and TP in manure (6000 mg kg⁻¹) were consistent with values reported elsewhere for dairy manure from the same source (Kleinman et al., 2002a, 2002b). However, the manure WEP content of

Table 2. Dry matter content and concentration of total P (TP) and water-extractable P (WEP) in manure and plant samples with no freezing, one freeze–thaw cycle (FTC), and eight freeze–thaw cycles.

Treatment	Manure			Plant		
	Dry matter	TP	WEP	Dry matter	TP	WEP
	%	— mg kg ⁻¹ —		%	— mg kg ⁻¹ —	
No freezing	15	6000	670	12	5800	50
1 FTC	nd†	nd	730	10	6300	2580
8 FTC	nd	nd	720	10	5700	6170

† Not determined.

670 mg kg⁻¹ measured in this study was substantially lower than the WEP of other dairy manures, such as 1250 mg kg⁻¹ reported by Kleinman et al. (2002b). This discrepancy may be caused by the lower solution/solids ratio (84:1) used in the current study, which is expected to extract less P from manure than the higher ratio reported by Kleinman et al. (2002b).

The harvested ryegrass contained 12% dry matter (Table 2), which is relatively low owing to the short period (21 d) of growth and immature growth stage. Total P concentration in the ryegrass was 5800 mg kg⁻¹ dry matter, nearly the same as in the dairy manure, whereas WEP in fresh biomass (undried) was only 50 mg kg⁻¹, <1% of TP. Ulén (1997) evaluated a ryegrass catch crop grown under field conditions and recorded a TP content of 4000 mg kg⁻¹ dry matter. Catch crop dry matter production in the runoff boxes was 180 g m⁻² (1800 kg dry matter ha⁻¹), which is higher than field observations of dry matter production (450–1240 kg ha⁻¹; Ulén, 1997; Bergström and Jokela, 2001; Molteberg and Tangsvén, 2002). This difference probably reflects optimum growth conditions in our study, which differs from field conditions with respect to temperature, moisture, the length of growing period and hence, growth stage of the plants. The optimal growth conditions for our box study give a higher risk of P release from catch crop than for field conditions and hence represent the potential for risk of P release.

Incubation Experiment

Before Freezing

Addition of manure to the two soils produced different trends in WEP and Mehlich-3 P, measured 21 d after incubation at 25 to 35°C (Table 3). Application of manure at 40 and 80 kg TP ha⁻¹ did not increase the WEP of the soils. However, Mehlich-3 P values increased significantly with manure application of 80 kg TP ha⁻¹. It is well established that mixing of soil with manure promotes sorption of soluble P in manure (Rajan and Fox, 1972; Griffin et al., 2003). Sharpley (1982) found that 90% of P that was potentially sorbed by soil was sorbed within 21 d of P application, the same period as the incubations conducted for the current study. Recent research by Sharpley et al. (2004) suggests that long-term application of manure to acidic soils increases the formation of Ca–P compounds, which are relatively insoluble in water extracts but are readily dissolved by the acidic Mehlich-3 extracting solution. It is possible that

Table 1. Properties of Watson and Berks soils used in the study.

Parameter	Watson	Berks
Clay content, %	33	21
CEC, cmol _c kg ⁻¹	12.4	13.0
pH	5.9	5.8
Total C, g kg ⁻¹	17	26
Field moist water content (10 kPa), g kg ⁻¹	310	350
Mehlich-3 P, mg kg ⁻¹	100	110

Table 3. Concentration of water-extractable P (WEP) and Mehlich-3 P in soil with different freeze-thaw treatments and two levels of manure application ($n = 3$). Standard deviation in parentheses.

Treatment	Manure					
	Bare soil		40 kg P ha ⁻¹		80 kg P ha ⁻¹	
	Watson	Berks	Watson	Berks	Watson	Berks
	mg kg ⁻¹					
	Water-extractable soil P					
No freezing	4.8 (0.29)	6.1 (0.84)	3.8 (0.27)	4.6 (0.45)	4.4 (0.13)	4.7 (0.41)
1 FTC‡	4.5 (0.25)	5.7 (0.75)	4.3 (0.37)	5.2 (0.15)	4.5 (0.49)	5.0 (0.49)
8 FTC	4.6 (0.69)	5.4 (0.19)	3.9 (0.15)	5.5 (0.42)	4.3 (0.50)	5.2 (0.40)
LSD _{α=0.05}	0.9	1.3	0.7	0.9	0.8	1.1
	Mehlich-3 extractable soil P					
No freezing	102 (0.6)	110 (9.4)	100 (3.2)	107 (0.7)	112 (6.1)	114 (6.0)
1 FTC	107 (4.0)	111 (2.4)	97 (4.7)	111 (5.4)	113 (4.4)	112 (3.4)
8 FTC	105 (4.2)	111 (2.5)	107 (6.4)	110 (3.1)	119 (1.3)	110 (1.7)
LSD _{α=0.05}	7	12	12	9	11	10

this mechanism accounts for the discrepancies in WEP and Mehlich-3 P trends in the manure-amended soils.

Growing a catch crop resulted in significant increases in WEP and Mehlich-3 P of the upper soil layer compared with both bare soil and soil amended with manure (Table 4). Changes in Mehlich-3 P and WEP with catch crop establishment likely reflect contributions of P from catch crop roots, as greater root biomass was observed near the soil surface. Vertical differences in WEP were observed within the catch crop and manured soil treatments. For the catch crop, concentrations of WEP in the 0- to 1-cm layer were significantly greater than in sub-soil layers, consistent with the role of plant biomass as a source of WEP in surface soil. In the manured soil treatment, the reverse trend in WEP was observed with depth. The lowest concentrations of WEP were measured in the 0- to 1-cm soil layer (Table 4). The low WEP concentration in this upper soil layer may be a result of translocation of small amounts of P by irrigation after manure application. There were no significant differences in Mehlich-3 P concentration for soil layers of the bare soil and manured treatments (Table 4).

Trends following Freezing and Thawing

Freezing and thawing did not significantly change WEP concentrations of the incubated manures, nor did it change the TP content of the manure and catch crop. However,

WEP associated with catch crop biomass increased significantly and profoundly with freezing and thawing (Table 2). In fresh plant material an average of 0.9% of TP was water extractable, whereas in frozen and thawed plant material WEP was greater than 40% of TP. Water-extractable P concentration of the catch crop increased logarithmically with the number of FTCs, appearing to plateau after approximately six FTCs (Fig. 1). By eight FTCs, the WEP of the catch crop was equivalent to the TP content (Table 2), indicating that all the P in the catch crop was converted to a water-soluble form. Rupturing of plant cells most likely caused the release of WEP from plant material.

Compared with other studies, the increase in WEP related to freezing and thawing in the current study was quite high. For instance, Miller et al. (1994), in a field study where mature plants were collected immediately after the first freeze, 15% of TP in plants was released to simulated runoff. In the current study, approximately 40% of TP was extracted with water after one FTC. It is likely that adaptation of plants to cold climate under field conditions may reduce the frost damage to plants. Elsewhere, White (1973) found that freezing increased nutrient release if plants are growing when frozen. Therefore, the abrupt changes in temperature (from about 10 to -18°C) in our experiment may have increased the effect of freezing. It may be that perennial plants in late autumn release

Table 4. Content of water-extractable P and Mehlich-3 P in soil layers (0–1, 1–3, and 3–5 cm) of the Watson soil before and after freezing (eight FTCs) of soil with catch crop, manure, and bare soil ($n = 3$). Standard deviation in parentheses.

Soil depth cm	Bare soil		Manure		Catch crop	
	Before freezing	After freezing	Before freezing	After freezing	Before freezing	After freezing
	mg kg ⁻¹					
	Water-extractable soil P					
0–1	4.5 (1.4)	3.7 (0.6)	3.7 (0.7)	4.2 (1.5)	12.5 (1.5)	9.1 (1.0)
1–3	5.8 (2.7)	3.9 (0.04)	7.7 (2.4)	7.0 (0.6)	6.9 (0.4)	6.6 (1.7)
3–5	6.9 (1.6)	5.8 (0.4)	8.8 (1.6)	8.5 (0.4)	7.9 (0.5)	6.5 (0.8)
Weighted mean	6.0	4.6	7.4	7.0	8.4	6.8
LSD _{α=0.05}	4.9	1.0	4.3	2.4	2.4	3.1
	Mehlich-3 extractable soil P					
0–1	102 (7.5)	94 (0.3)	110 (1.7)	108 (3.5)	115 (6.9)	97 (5.1)
1–3	103 (3.8)	107 (1.9)	105 (2.2)	109 (10)	93 (4.7)	90 (8.6)
3–5	111 (3.4)	103 (2.6)	109 (7.3)	111 (4.6)	90 (1.6)	80 (5.6)
Weighted mean	106	103	108	110	96	88
LSD _{α=0.05}	13	4	11	17	12	17

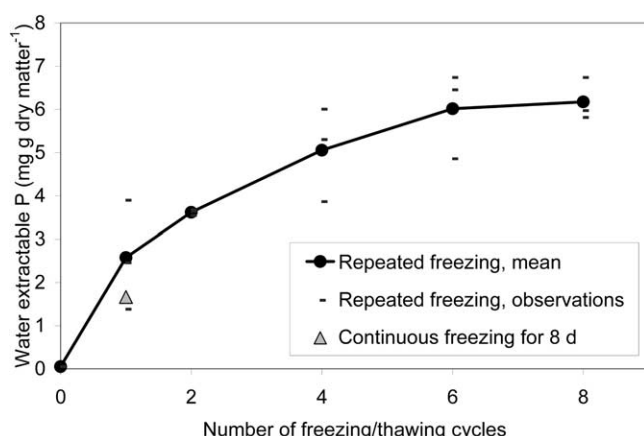


Fig. 1. Water-extractable P in annual ryegrass exposed to different number of freeze–thaw cycles (FTC). Repeated freezing (1 FTC/d); Continuous freezing (8 d).

less P from aboveground plant parts than do the growing annual catch crops. Molteberg et al. (2004) showed that most of the P loss from annual and perennial ryegrass in Norway occurred during late winter, though more frequent FTCs occurred in early winter. They concluded that differences in physiology of plants prepared for winter compared with plants starting their growth in early spring were responsible for this difference, the latter being more susceptible to freezing. Hence, results of the current study can be viewed as describing a maximum potential for P release from catch crops.

Continuous freezing of catch crop plant material (1 FTC/8 d; Fig. 1) resulted in lower WEP from the catch crop compared with repeated freezing and thawing (1 FTC/d; Fig. 1) during the same time period. Freezing of intracellular solutes causes disruption of cells (White, 1973). Because of variation in physiology of plant cells, not all cells are disrupted by one freezing. Subsequent thawing causes changes in the plant cells and by the next freezing additional plant cells will be disrupted (O.H. Baadshaug, personal communication, 2004). Thus, the current study points to a potential increase in the release of plant P to water with increasing FTCs.

Freezing of the boxes with catch crop caused a significant reduction in WEP and Mehlich-3 P in the upper 1 cm and the 3- to 5-cm layers (Table 4). However, the WEP concentration of the upper soil layers of the catch-cropped soils was still higher than for bare and manured soils. There was no effect of freezing on WEP and Mehlich-3 P in the middle soil layer (1–3 cm) (Table 4). This suggests that although the boxes were insulated, the speed of freezing may have varied for different layers and differentially influenced soil P extractability (Vaz et al., 1994). The reduction in labile soil P fractions (Mehlich-3 P and WEP) in the catch-cropped soil after freezing may be attributed to sorption by soil of part of the P released from disrupted roots of the crop.

Runoff Experiment

Trends before Freezing

Concentrations of TP in runoff from the catch-cropped boxes were approximately one-fourth of those from bare

Table 5. Dissolved reactive P (DRP), total P (TP), and suspended sediments (SS) in runoff from Watson soil receiving different treatments of freezing and soil management ($n = 2$). Standard deviation in parentheses.

Soil management	Runoff volume $L\ 30\ min^{-1}$	DRP	TP	SS
		$mg\ L^{-1}$		$g\ L^{-1}$
		Not frozen		
Catch crop	3.3	0.10 (0.04)	0.49 (0.2)	0.04 (0.03)
Manure	2.9	0.14 (0.04)	2.02 (0.7)	1.45 (0.6)
Bare soil	2.7	0.09 (0.02)	1.72 (0.8)	1.28 (0.5)
		Runoff from frozen soil		
Catch crop	3.2	9.7 (1.6)	17.9 (4.0)	0.59 (0.3)
Manure	2.7	0.18 (0.03)	3.25 (0.9)	1.33 (0.3)
Bare soil	2.8	0.14 (0.04)	2.42 (0.4)	0.96 (0.2)
		Runoff from thawed soil		
Catch crop	2.6	10.3 (1.6)	17.9 (7.6)	0.57 (0.2)
Manure	2.8	0.13 (0.03)	2.59 (0.8)	1.06 (0.9)
Bare soil	3.0	0.13 (0.03)	2.59 (0.8)	1.06 (0.9)

and manured soils, which did not differ significantly (Table 5). As illustrated in Fig. 2, TP concentrations in runoff from bare and manured soils were closely related to concentrations of SS, indicating that soil erosion was the dominant cause of P loss in runoff for those treatments. As with TP, concentrations of SS in runoff from the catch crop treatment were significantly lower than in runoff from the bare and manured soil treatments, confirming the widely reported benefit of catch crops in controlling erosion (Sharpley and Smith, 1991). Lundekvam (2002) estimated a 25% smaller soil loss for catch-cropped areas compared with no-till in autumn without catch crop.

Concentrations of DRP in runoff from the three soil management treatments were not significantly different (Table 5). Other studies have reported varying effects of manure incorporation on DRP in runoff. Sharpley (1995) amended soils with different rates of poultry litter to achieve a broad range of soil P concentrations, which, in turn, were correlated with DRP in runoff. Kleinman et al. (2002a) observed no increase in concentrations of DRP in runoff after mixing manure with soil. The lack of difference in runoff concentrations of DRP from catch

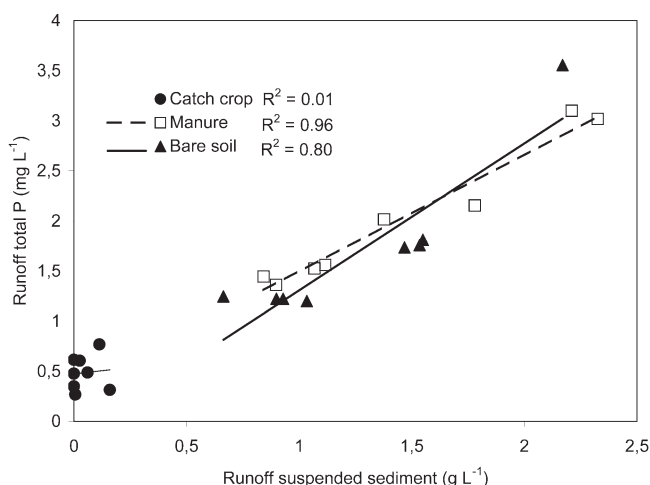


Fig. 2. The relationship between total P in runoff and suspended sediments in runoff before freezing of the catch-cropped, manured, and bare soil runoff boxes.

crop and bare soil boxes before freezing would appear to differ with the findings of Sharpley (1981), who found that DRP from plants contributed 56 to 84% of TP in runoff. In that experiment, however, runoff water did not interact with soil, and DRP concentrations were approximately one-tenth of those measured in the current study. It is likely that the high P contents of the Watson and Berks soils and related, elevated soil P release to runoff may have masked any effect of plant P release on runoff DRP.

Trends following Freezing

Freezing and thawing had little effect on runoff water quality of manured and bare soil treatments (Table 5). These findings are consistent with the soil incubation experiment where no changes in soil WEP and Mehlich-3 P were observed following freezing and thawing of bare and manured soils (Table 3). Nor were differences observed in runoff from soils that were frozen vs. those that had been frozen and then were thawed for 12 h (Table 5). However, the freezing treatments produced a profound increase in DRP concentrations in runoff from the catch cropped soil. From these soil boxes, runoff concentrations of DRP increased approximately 100-fold over prefreezing concentrations (Table 5), paralleling the large increases in biomass-related WEP reported above (Fig. 1 and Table 4). These findings are supported by the field observations of Ulén (1997), where increases in dissolved P in runoff after freezing of unfertilized grasses were observed. Concentrations of DRP reported by Ulén (1997) were substantially lower than in the current study, reflecting differences between field conditions (plant maturity, freeze-thaw characteristics, and rainfall-runoff intensity) and conditions simulated in this study. Nevertheless, combined, the findings of this study and those of Ulén (1997) provide compelling evidence for significant exacerbation of DRP losses with catch crops grown in frigid regions.

As summarized in Table 5, concentrations of TP and SS also increased significantly after freezing the catch crop treatment, pointing to increased erosion or a greater loss of plant material in runoff after freezing. In fact, though runoff DRP concentrations were greatly elevated after freezing, they accounted for only 54 to 58%

of TP in runoff. It is important to note that the concentration of SS in runoff from the catch-cropped treatment after freezing remained significantly lower than in runoff from bare and manured soil treatments (Table 5), indicating continued erosion control benefits of the catch crop even after freezing and thawing.

Leaching Experiment

Trends before Freezing

Before freezing, no significant differences were detected in leachate DRP from any of the bare and catch-cropped soils (Table 6). Dissolved reactive P accounted for an average of 44% of TP in leachate from both soils, suggesting substantial contribution of particulate P and/or dissolved organic P to TP in leachate. Other studies have highlighted the potentially important role of organic P and particulate P in subsurface P transport (e.g., Chardon et al., 1997; Stamm et al., 1998; Stevens et al., 1999). Surprisingly, significantly greater concentrations of TP were found in the leachate from the bare Watson soil than from the catch-cropped Watson soil. It is possible that dispersion of surface aggregates by direct impact of raindrops onto the bare soil and translocation of fine sediments via macropores contributed to this difference. Indeed, the contribution of DRP to TP in Watson leachate was 58% from the bare soil and 41% from the catch-cropped soil, consistent with a greater contribution of particulate P in leachate from the bare soil than in leachate from the catch-cropped soil. However, the small size of the difference in TP concentrations (0.05 mg L^{-1}) and the absence of a similar difference in leachate TP from the Berks soil suggest caution in over-interpreting these results.

Trends following Freezing

Freezing of the soil columns did not significantly affect DRP and TP in leachate from the Watson soil, nor did freezing affect DRP in leachate from the Berks soil (Table 6). However, TP in leachate from the Berks soil did decline significantly from before to after the freezing. This suggests a drop in the translocation of P-enriched surface particles in leachate from the Berks soil with repeated freezing and thawing. It is possible that freezing and thawing resulted in aggregate breakdown (Formanek et al., 1983; Bullock et al., 1988; Øygarden, 2000) and collapse of continuous macropores that served as conduits for particles from the soil surface in leachate. Indeed large macropores ($>2 \text{ mm}$), some containing roots, were observed at bottom of all lysimeters (Berks and Watson), some of which may have been continuous with the soil surface, and Kleinman et al. (2005) identified large numbers of continuous macropores up to a depth of 50 cm in similar soils using a dye-tracer. However, if this mechanism explains the drop in leachate TP from the Berks columns, it is unclear why a similar trend was not observed in the Watson columns (Table 6).

No significant differences were observed between catch crop and bare soil treatments after freezing. Surface application of manure did not significantly increase

Table 6. Total phosphorus (TP) and dissolved reactive phosphorus (DRP) in leachate from Watson and Berks soil receiving different freezing treatments and manure application (80 kg P ha^{-1}) ($n = 2$). Standard deviation in parentheses.

Soil management	DRP		TP	
	Watson	Berks	Watson	Berks
mg L^{-1}				
Leaching before freezing				
Bare soil	0.10 (0.05)	0.11 (0.07)	0.17 (0.03)	0.32 (0.26)
Catch crop	0.05 (0.01)	0.08 (0.03)	0.12 (0.03)	0.17 (0.08)
Leaching after eight FTCs				
Bare soil	0.08 (0.07)	0.02 (0.01)	0.31 (0.29)	0.02 (0.01)
Catch crop	0.02 (0.01)	0.07 (0.07)	0.14 (0.03)	0.07 (0.03)
Leaching after manure application				
Unmanured	0.03 (0.02)	0.06 (0.06)	0.08 (0.04)	0.18 (0.1)
Manured	0.07 (0.03)	0.57 (0.88)	0.19 (0.11)	0.87 (1.1)

P in leachate from the Berks soil after freezing, primarily due to large variances between replications, but produced significant increases in leachate TP from the Watson soil (Table 6). Elsewhere, Kleinman et al. (2005) observed that leachate P was greater from a Buchanan soil (similar to the Watson soil in the current study) after manure addition than from a Hartleton soil (similar to the Berks soil). Results of Kleinman et al. (2005) and the current study highlight the potential of some fine-textured soils to convey surface-applied manure P to the subsoil.

CONCLUSIONS

This study shows that growing catch crops with the intent of controlling losses of N and erosion can increase dissolved P runoff. Concentrations of SS in surface runoff from catch-cropped soils were reduced to 2% of those in the other soil treatments, with lower SS in runoff from catch-cropped soils continuing after repeated FTCs. However, elevated DRP concentrations in runoff from catch crops exposed to freeze–thaw conditions, increased surface runoff P above that observed from bare and manured soils. Concentrations of TP in runoff were increased 100 times by freezing the catch-cropped soil boxes. Higher WEP content in the surface of the catch-cropped soil and release of P from catch crop plants contributed to the increased P losses. Release of P from plant material increased with increasing number of FTCs. Catch crops did not contribute to elevated leaching losses of P from the two moderately textured soils included in this study. Leaching of P through small soil columns was not increased by freezing of the catch crop. This study highlights the trade-offs in promoting catch crops for control of nonpoint-source nutrient P.

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